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Gravimetry

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Weapons Systems Division
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ABSTRACT

In 1986, Bulusu et al. (*J. Phys. Chem.*, **90** 4121-4126) reported on the kinetics of the thermal decomposition of HMX at atmospheric pressure from 508 K to 555 K, using isothermal gravimetric analysis. Their work implied that the decomposition kinetics followed a simple Arrhenius temperature - rate law dependency but their analysis did not describe the actual kinetic pathway in any detail.

In the present study, some key experiments were repeated. As a result, the following points, most of which are pertinent to any mechanistic discussion but were not considered in Bulusu's paper, can be made:-

a) Over the entire temperature range of the Bulusu study, HMX exists not in its β - polymorphic form but in its δ - form.

b) The thermal decomposition of δ -HMX follows a reaction rate law which fits a sigmoidal α -t relationship of the form $d(\alpha)/dt = k' \alpha (1 - \alpha)$, where k' is the kinetic rate constant, α is the fractional extent of the reaction and t is the time.

c) This reaction proceeds with the complete loss of mass in the form of volatile products.

d) Over the temperature range 508 K to 524 K, the kinetics follow an Arrhenius relationship, the Arrhenius pre-exponential, $\ln A$ (min^{-1}), over this temperature range having a value of 31.07 and the energy of activation, E_a , a value of 144 kJ mol^{-1} . However, somewhere beyond 524 K, a decomposition reaction with a different Arrhenius dependency probably comes into play - the rate of reaction observed at 539 K being much greater than that calculated using the lower temperature-range Arrhenius parameters.

The mechanistic implications of this study are placed in the context of information from other studies.

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Executive Summary

The cyclic nitramines, HMX and RDX, have been used in a wide variety of propellant and high explosive formulations for many years but, surprisingly, very few studies have addressed the relationship between kinetic data and product formation.

An understanding of the complex physicochemical processes which underlie the combustion of these nitramines can provide a link between basic scientific data and their combusive behaviour as well as leading to methods of assessing the effects of modifying the basic formulations. In this report, the authors have chosen to reassess the published kinetic data on the thermal decomposition of HMX below its ignition temperature and to comment on mechanistic aspects of the reactions so observed.

It has been found that

a) the thermal decomposition of δ -HMX follows a reaction rate law which fits a sigmoidal α - t relationship of the form

$$d(\alpha)/dt = k' \alpha (1 - \alpha),$$

where k' is a bimolecular rate constant characteristic of the reaction, α is the fractional extent of the reaction and t is the time,

b) this reaction proceeds with the complete loss of mass in the form of volatile products, and

c) in the temperature range close to the ignition temperature of HMX, 508 K to 524 K, the kinetics follow an Arrhenius relationship. The Arrhenius pre-exponential, $\ln A$ (min^{-1}), has a value of 31.07 and the corresponding energy of activation, E_a , has a value of 144 kJ mol^{-1} .

In other studies carried out elsewhere, it appears as if the major products of the very early reactions of the thermal decomposition are formaldehyde (H_2CO) and nitrous oxide (N_2O), formed in very similar relative amounts. These may be associated with rupture of the HMX ring and subsequent "unzipping" of the HMX molecular framework. Such an observation does not preclude the rupture of the nitramine N-N bond, the weakest bond in the system, to yield nitrogen dioxide (NO_2 or N_2O_4) but rather suggests that, if N-N bond rupture is implicated in the first step, other processes rapidly take over.

The tie-up between the kinetic profile and the pathway of the reaction is an important one, all the more so because such information will be required as input data for future modelling studies.

Authors

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1. Introduction

Recently, Brill *et al.* [1] rationalised the often-disparate results [2] obtained from the numerous kinetic studies on the rate laws and Arrhenius kinetic parameters operating in thermal decompositions of HMX, RDX and NTO at atmospheric pressure (1 atmos. = 0.101325 MPa). In essence, Brill reported that the global reaction kinetic measurements of the thermal decompositions of these molecules (and, no doubt, many others) are strongly affected by sample characteristics and experimental conditions but that often a compensating relationship exists between the observed Arrhenius pre-exponential factor, A , and the observed activation energy, E_a . This compensating relationship has its origins in considerations of the overall free energy changes occurring in a reaction and its influence on reaction rates and reaction pathways [3, 4].

For HMX, this relationship can be expressed in a simple form [1], namely

$$\ln A (\text{min}^{-1}) = 0.2252 E_a (\text{kJ mol}^{-1}) - 1.4222 \quad [\text{Eq. 1}]$$

with the coefficient of determination, R^2 , equal to 0.9693.

This prompted the present authors to look more closely at some of their own unpublished results on HMX at atmospheric pressure in the solid state and to compare them with those which were published by Bulusu *et al.* [5] but not mentioned in Brill's paper. This report reassesses the Bulusu data; it adds a global kinetic rate law to the Bulusu explanation, reevaluates the kinetic rate constants in a form which is seen to correlate with that expected from Brill's report and draws attention to the status of the kinetic picture with the products observed from the thermal decomposition reactions.

2. Experimental

A research sample of pure HMX was given to Dr. Robert Spear, Explosives Division, Materials Research Laboratory (the forerunner of Weapons Systems Division, Aeronautical and Maritime Research Laboratory) in 1988 by the US Army Armament Research and Development Center (ARDEC), Dover, New Jersey, USA. This is the same laboratory from which Bulusu published his report and it is possible that the HMX sample was from either the same, or similar, stock used by Bulusu in his work. This is mentioned only in as far as it is relevant to the suggestion implied in the Introduction [1, 2] that variations in particle size can have an effect on the kinetics of the thermal decomposition of HMX.

A sample of this HMX was examined under a scanning electron microscope (Fig. 1) revealing that the material was composed of large crystals, the mean dimensions of which were (approx.) 0.58 mm long, 0.24 mm wide and 0.18 mm high; these dimensions were estimated from a computer-based stereo examination, carried out by Mr. Ian McDermott (Image Analysis Group, MRL, 1990), of approx. 80 representative crystals, chosen at random.

Isothermal gravimetric analysis (ITGA) on this material in the solid state was carried out in a stream of nitrogen (100 mL / min) at 515.4 K (242.4 °C) and at 524.2 K (251.2 °C), on a Stanton Redcroft Simultaneous Thermal Analyser Model 1500, controlled by appropriate software.

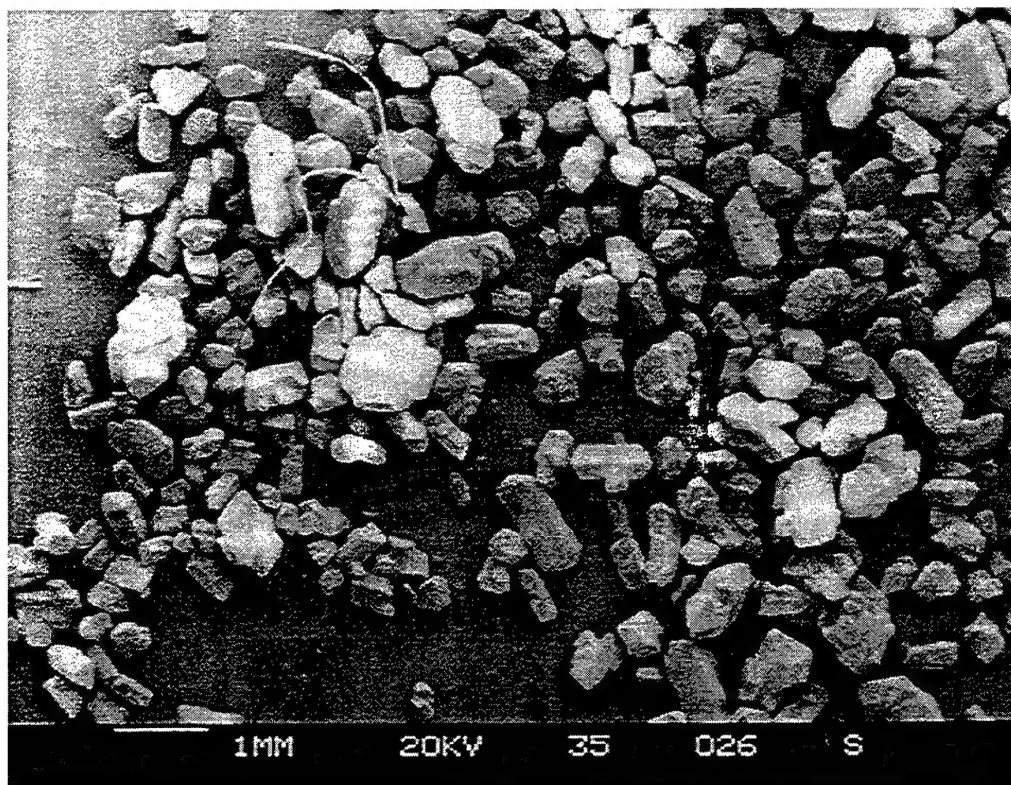


Figure 1: An electron micrograph of the sample of α -HMX obtained from US Army Armament Research and Development Center (ARDEC) and used in this study.

At ambient temperature and pressures close to atmospheric pressure, HMX exists in its most dense form, the β - polymorph. Under a similar pressure but at a temperature of 458 K (185 °C), it transforms completely into the less dense, δ -polymorph in less than 7 mins. [6], a change which can be completely reversed by applying elevated pressures (300 - 380 atmos., 30 - 38 MPa) on the heated sample [6-8]. It is therefore apparent that the current study was one involving the decomposition of δ - HMX.

From DSC measurements carried out in the non-isothermal or dynamic mode at a heating rate of 10 K min^{-1} , our sample of HMX started to decompose, albeit slowly, above ca. 540 K (267°C). The principal exotherm commenced near 545 K with an extrapolated onset temperature of 553 K and it reached a maximum rate of evolution of heat at 554 K . From a series of DSC runs at heating rates from 5 to 20 K min^{-1} the measured heat of reaction was found to be $1400 \pm 60 \text{ J g}^{-1}$.

In the temperature range, 505 K to 540 K , our sample of HMX appeared to be free of any identifiable endothermic/exothermic phase transitions.

3. Results

The ITGA traces from HMX at 524.2 K (251.2°C) followed the well-established sigmoidal mass loss / time profile [9-13], in which the total mass of HMX underwent thermal decomposition to volatile products (Table 1). A similar trace, albeit from a slower reaction, was obtained from HMX at 515.4 K .

Table 1. *The Mass Loss in terms of the Extent of Reaction (α) vs. Time for the Isothermal Decomposition at 524.2 K of HMX in covered (but not crimped) aluminium sample pans in a stream of nitrogen. Mass of sample: 0.607 mg .*

Time (min.)	α	$\ln [\alpha / (1 - \alpha)]$	Time, min	α	$\ln [\alpha / (1 - \alpha)]$
24	0		50	0.419	-0.32688
26	0.007	-4.95482	52	0.475	-0.10008
28	0.018	-3.99922	56	0.589	0.35983
30	0.033	-3.37769	60	0.695	0.82360
34	0.072	-2.55637	62	0.741	1.05117
38	0.118	-2.01151	64	0.785	1.29505
42	0.199	-1.39256	68	0.860	1.81529
46	0.313	-0.78613	72	0.924	2.49798
48	0.365	-0.55373	76	0.976	3.70541

The Linear Least Squares plot of $\ln [\alpha / (1 - \alpha)]$ vs. t (min.) fits [Eq. 2b], as presented in the form $\ln [\alpha / (1 - \alpha)] = -7.00709 + 0.13128 t$ (min.), with a LLSQ coefficient of determination of 0.99277 , for $0.033 < \alpha < 0.86$

The data from both of these traces could be fitted satisfactorily to a rate law of the form

$$\text{Velocity, or time rate of reaction, } v = d(\alpha) / dt, \text{ and}$$

$$d(\alpha) / dt = k' \alpha (1 - \alpha) \quad [\text{Eq. 2a}],$$

for $0.05 < \alpha < 0.86$, where α is the fractional extent of reaction.

In integrated form, [Eq. 2a] becomes

$$k' (t - t_{0.5}) = \ln [\alpha / (1 - \alpha)] \quad [\text{Eq. 2b}],$$

where $t_{0.5}$ is the notional time at which $\alpha = 0.5$.

At 524.2 K, the rate constant, k' , had the value 0.13128 min^{-1} (Table 1). This value of k' and that obtained at the lower temperature, 515.4 K, 0.07229 min^{-1} , appeared to be considerably higher than those reported by Bulusu [5].

The features of a sigmoidal fractional extent of reaction (α) vs. time (t) plot following Eq. 2 are such that, in the domain $0.4 < \alpha < 0.6$, the velocity (or rate of reaction) varies from 96 % v_{\max} (at $\alpha = 0.4$ and 0.6) to v_{\max} (at $\alpha = 0.5$). This may appear, at first sight, to be a domain of constant velocity - but, in reality, it is not.

$$\text{From Eq. 2a,} \quad k' = 4 v_{\max} \quad [\text{Eq. 3}]$$

In Bulusu's treatment of the experimental data, he apparently assumed that the central portion of the sigmoidal α vs. time plot was linear and he defined his rate constant (which the present author has labelled k^{app}) as a zero-order rate constant. If one further assumes Bulusu determined k^{app} in the time domain from $\alpha = 0.4$ to 0.6 , then

$$k^{\text{app}} = \delta \alpha / \delta t = [0.6 - 0.4] / [t(0.6) - t(0.4)] \quad [\text{Eq. 4}],$$

which is 96 % v_{\max} . Accordingly, the true value of the rate constant, k' , which is of second order, is given by

$$k' = 4 v_{\max} = 4 k^{\text{app}} / 0.96 \quad [\text{Eq. 5}],$$

and the kinetic data in Bulusu's paper can be recalculated to give the true mechanistic rate constant, k' , rather than the pseudo-rate constant, k^{app} (Table 2).

From the recalculated Bulusu data for the temperature range 508 K to 522.6 K, one finds from an Arrhenius plot the pre-exponential term, $\ln A (\text{min}^{-1})$, has a value of 31.07 and the energy of activation, E_a , 144 kJ mol^{-1} ($34.5 \text{ kcal mol}^{-1}$). The calculated value of the RHS of Eq. 1 becomes 31.074, a value of $\ln A (\text{min}^{-1})$, to all intents and purposes, identical with that from the Arrhenius plot.

Table 2. *Experimental Autocatalytic Rate Constants, calculated from Eq. 2, for the Thermal Decomposition of δ -HMX in the true Solid State from TGA Experiments carried out by Bulusu [3] and by the present Authors.*

Temp. (°C)	Temp. (K)	k^{app} (min ⁻¹)	k' (min ⁻¹)
235.0	508.0	0.0104	0.04333
237.0	510.0	0.0122	0.05083
239.3	512.3	0.0151	0.06291
242.5	515.5	0.0203	0.08457
249.6	522.6	0.0267	0.11123
265.9	538.9	0.1174	0.489088
AMRL data	515.4		0.07229
	524.2		0.13128

A linear least squares Arrhenius plot of $\ln A$ (min⁻¹) vs. $1/T$ over the temperature range 508 K to 522.6 K yields a straight line with a coefficient of determination of 0.976, an intercept, $\ln A$ (min⁻¹), of 31.068 and gradient, $-E/R$, -17374.

From these Arrhenius values, the calculated rate constants for the reaction at 515.4 K and at 524.2 K were 0.07469 min⁻¹ and 0.13143 min⁻¹ respectively; these are values which are remarkably close to those obtained experimentally at AMRL, 0.07229 min⁻¹ and 0.13128 min⁻¹ (the last two entries of Table 2). On the other hand, we note that for the thermal decomposition at 538.9 K, the calculated value of k' on the basis of the cited Arrhenius parameters is 0.3242 min⁻¹; this compares to Bulusu's experimentally-obtained reassessed value, 0.4891 min⁻¹. Why the large difference? The reason may be experimental; alternatively, the thermal decomposition of HMX at this higher temperature may be proceeding from a discernibly-different pathway than at the lower temperature, though one with the same general, sigmoidal α vs. t appearance.

Actually, it was very tempting to include the kinetic data obtained at 265.9 °C (538.9 K) by Bulusu in the Arrhenius analysis above, more particularly so as a slightly better $\ln k'$ vs $1/T$ line-of-best-fit would have been obtained covering the spectrum of data from 508 K to 539 K. This, in turn, would have led to revised values for $\ln A$ (min⁻¹) of 38.01 and E_a , 174 kJ mol⁻¹ (41.5 kcal mol⁻¹).

However, in a parallel study, the present authors found that, in trying to duplicate Bulusu's work with a run at 540.1 K, thermal equilibrium could not be maintained between the sample and the reference. In short, self-heating of the sample (mass 0.6 mg) was occurring, raising the sample temperature erratically and above the nominal temperature of the reference compartment of the thermal analyser, thus rendering the interpretation of the experimental TGA data suspect.

The authors have previously met and reported on the problem of self-heating in isothermal DSC studies on strongly exothermic materials [11, 12]. For this reason, they have preferred to confine their considerations to results obtained over the narrower temperature range, 508 K to 522.6 K, where the sample is definitely at a constant temperature over the period of the reaction.

4. DISCUSSION

In isothermal thermal gravimetric analysis (ITGA), one measures the time rate of loss of mass from the sample pan at constant temperature. A chemist then tries to correlate this mass loss with a kinetic rate law (such as Eq. 2) and to rationalise the Arrhenius parameters describing the temperature dependence of the overall processes in terms of molecular phenomena (rate-determining steps in bond-rupture or bond-forming processes, lattice rearrangement or breakdown, etc.). In some studies this can be done; however, in most cases involving solid state reactions, one can only make a very general statement, namely:- over the temperature range studied, the reaction follows a particular rate law and, from the temperature dependence of the rate constant deduced from the rate laws, one can determine the Arrhenius parameters (activation energy and pre-exponential factor) for the overall reaction. These in turn reflect the overall free energy change associated with the reaction and, as such, provide accurate data for those who model complicated rate processes, such as explosive reactions, in detail [14]. This has been one justification for studying thermal decomposition reactions of energetic materials.

What is intriguing, however, is the fact that in thermal decomposition reactions such as studied here the *overall decomposition reactions may be very complicated even though the global kinetic picture* described in the previous paragraph appears quite simple [13, 15].

In this current study, it appears as if the kinetics of the thermal decomposition of δ -HMX over the temperature range 508 K to 522.6 K follow a bimolecular rate law which can be described mathematically in the form

$$d(\alpha) / dt = k' \alpha (1 - \alpha) \quad [\text{Eq. 2a}]$$

where the reaction proceeds with the complete loss of mass in the form of volatile products. In addition, the rate constant obeys an Arrhenius relationship with the pre-exponential term, $\ln A$ (min^{-1}), having a value of 31.07 and the energy of activation, E_a , 144 kJ mol^{-1} and these kinetic parameters appear to fit in with the linear free energy kinetic relationship, presented by Brill and his coworkers [1] and summarised by Equation 1.

The integrated form of the rate law, Eq. 2b, suggests that, overall, the reaction is characterised by an induction period, corresponding to the first 10 % of the reaction (from $\alpha = 0$ to $\alpha = 0.1$), a regime of rapid reaction (from $\alpha = 0.25$ to $\alpha = 0.75$) and a fading out phase ($\alpha = 0.9$ to $\alpha = 1$). Classically, the reaction begins under an

appropriate thermal stimulus at sites of strain within the crystal (be they defect centres, slip planes or lattice imperfections) [13, 16]; these are sites of high crystal free energy. As the reaction proceeds, the products of the reaction induce a change within the solid lattice with the introduction of more sites of high free energy and the reaction rate increases - the so-called autocatalytic effect implied by Eq. 2. Eventually, the character of the original solid matrix alters so significantly that the rate of decomposition of the remaining molecules becomes an isolated statistical event once again, but in a different crystal environment, and the rate of reaction slows down or fades away.

Support for this overall picture comes from kinetic studies [16-20] and from an examination of micrographs taken from residues of crystalline matrices which have undergone compositional change or from residues remaining from incomplete, quenched or interrupted reactions [13, 19-21].

Aspects of the mechanistic interpretation of the reactions involved in the thermal decomposition of HMX in the condensed state, in terms of product analyses and the variation of the products with time, have been addressed in recent times by Behrens, using mass spectrometry [13] and by Wight and Botcher [22] and Oyumi and Brill [23], both of whom used IR detection techniques.

From these studies, it is apparent that there are several different decomposition pathways occurring and the sigmoidal α vs time profile represents the sum total of the effects of all of these pathways. For that reason alone, the Arrhenius parameters have only a global significance and cannot be attributed to a specific reaction pathway.

According to Behrens,

- the major products for reactions between 483 K and 508 K (210 °C and 235 °C) appear to be nitric oxide (NO), formaldehyde (CH₂O), water (H₂O), nitrous oxide (N₂O), and carbon monoxide (CO);
- minor amounts of hydrogen cyanide (HCN), dimethyl nitrosamine, (Me₂N-NO), monodeoxygenated HMX(ON-TNTA, 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine), an amidic product and a polymeric residue (ca. 4 % by mass of the original material) were also identified. No residual material was observed in the study reported here.
- during the induction period, the formation of nitrous oxide (N₂O) and formaldehyde (CH₂O) in very similar relative amounts predominated, while, in the regime of the most rapid part of the reaction, all of the products - be they minor or major- were identifiable. With the passage of time, secondary reactions not directly part of the thermal decomposition reaction appeared to be occurring between some of the gaseous products.

This suggests that, in the induction period, ring opening (with C-N bond rupture) and probable "de-zipping" of HMX occurs, to yield N₂O and CH₂O; it does not preclude other reactions or the role of other reactions (like nitramine N-N bond rupture) in actually initiating the decomposition process.

Oyumi and Brill [23] studied the thermal decomposition of HMX under a whole variety of conditions; in Fig. 8 of their paper [23], they presented a concentration - time profile of the gaseous products from HMX under an atmospheric pressure of nitrogen, heated to 558 K (285 °C) at a heating rate of 40 K min⁻¹. Here, HCN, CH₂O, N₂O and NO₂ were the principal initial products; this was interesting as Behrens reported that his techniques did not identify HCN except as a minor product and that it appeared later in the reaction sequence. Perhaps, in the time-of-flight mass spectrometer, HCN may undergo a secondary reaction and appear harder to detect.

Secondary reactions [24] may just confuse the issue.

Just one thing remains to be said on this matter; the formula weight of CH₂O is 30 atomic mass units (amu). This is also the formula weight of NO. Therefore, should one ask if it is possible that NO and CH₂O could be confused in the mass spectrometric analysis. Vibrationally-hot NO₂, *NO₂, from nitramine N-N bond rupture could then be the precursor to the e/m peak at 30 amu, per medium of either a unimolecular reaction or multi-body collision



where M is an unspecified reactant or reaction site.

Wight and Botcher have already pointed out that, in RDX and HMX, the nitramine N-N bond is the weakest bond in the system; this implies that NO₂ may be expected to be a primary reaction product. These same authors have also reported that the IR spectrum of a thin film of N₂O₄ (dimeric NO₂) is very similar to that of CH₂O in the 1800-1700 cm⁻¹ region and it is possible that an incorrect assignment could be made, unless one was very careful.

Were further work to be done studying the thermal decomposition of HMX by isothermal TGA, the authors would suggest that such a study investigate the effects of crystallinity and of particle size of HMX on the kinetics, as a first step. Other experiments would naturally stem from the results thus obtained.

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Daniel J Whelan and Mark R Fitzgerald

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19. ABSTRACT In 1986, Bulusu et al. (<i>J. Phys. Chem.</i> , 90 4121-4126) reported on the kinetics of the thermal decomposition of HMX at atmospheric pressure from 508 K to 555 K, using isothermal gravimetric analysis. Their work implied that the decomposition kinetics followed a simple Arrhenius temperature - rate law dependency but their analysis did not describe the actual kinetic pathway in any detail. In the present study, some key experiments were repeated. As a result, the following points, most of which are pertinent to any mechanistic discussion but were not considered in Bulusu's paper, can be made:- a) Over the entire temperature range of the Bulusu study, HMX exists not in its β - polymorphic form but in its δ - form.					

b) The thermal decomposition of δ -HMX follows a reaction rate law which fits a sigmoidal α -t relationship of the form $d(\alpha)/dt = k' \alpha (1 - \alpha)$, where k' is the kinetic rate constant, α is the fractional extent of the reaction and t is the time.

c) This reaction proceeds with the complete loss of mass in the form of volatile products.

d) Over the temperature range 508 K to 524 K, the kinetics follow an Arrhenius relationship, the Arrhenius pre-exponential, $\ln A$ (min^{-1}), over this temperature range having a value of 31.07 and the energy of activation, E_a , a value of 144 kJ mol^{-1} . However, somewhere beyond 524 K, a decomposition reaction with a different Arrhenius dependency probably comes into play - the rate of reaction observed at 539 K being much greater than that calculated using the lower temperature-range Arrhenius parameters.

The mechanistic implications of this study are placed in the context of information from other studies.